

Isothermal and Adiabatic Elastic Tensors

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Abstract

The adiabatic elastic modulus is often useful in the high frequency response of materials. Unfortunately, it can be much more difficult to directly measure the adiabatic elastic modulus of material than the isothermal elastic modulus. We derive the relationship between the adiabatic and isothermal elastic tensors from the first law of thermodynamics.

1 Notation

σ_{kl} = Stress Tensor

ε_{ij}^o = Strain Tensor, includes both stress-induced and temperature-induced strain

T = Temperature

S = Entropy

U = Internal Energy

H = Enthalpy

p = Pressure

V = Volume

α_{ij} = Coefficient of Thermal Expansion

C_{ijkl} = Stiffness Tensor

S_{ijkl} = Compliance Tensor

$c_{\sigma_{ij}}$ = Heat Capacity at Constant Stress

$c_{\varepsilon_{ij}^o}$ = Heat Capacity at Constant Strain

2 Definitions

2.1 Heat Capacity

With liquids, there are two possible heat capacities which can be defined, one at constant pressure and one at constant volume. We are defining an analogous pair of heat capacities at constant stress and at constant strain. The constant strain heat capacity is defined as:

$$\left(\frac{\partial U}{\partial T}\right)_{\varepsilon_{ij}^o} \equiv c_{\varepsilon_{ij}^o} \quad (1)$$

The constant stress heat capacity is defined as:

$$\left(\frac{\partial H}{\partial T}\right)_{\sigma_{ij}} \equiv c_{\sigma_{ij}} \quad (2)$$

2.2 Thermal Expansion

The differential strain of a material is defined by changes in temperature and stress state.

$$d\varepsilon_{ij}^o \equiv \left(\frac{\partial \varepsilon_{ij}^o}{\partial T}\right)_{\sigma_{kl}} dT + \left(\frac{\partial \varepsilon_{ij}^o}{\partial \sigma_{kl}}\right)_T d\sigma_{kl} \quad (3)$$

The thermal expansion coefficient is defined at constant stress state.

$$\left(\frac{\partial \varepsilon_{ij}^o}{\partial T}\right)_{\sigma_{kl}} \equiv (\alpha_{ij})_{\sigma_{kl}} \quad (4)$$

2.3 Isothermal Stiffness and Compliance

The isothermal stiffness tensor is defined as:

$$\left(\frac{\partial \sigma_{ij}}{\partial \varepsilon_{kl}^o}\right)_T \equiv C_{ijkl} \quad (5)$$

Correspondingly the isothermal compliance is defined as:

$$\left(\frac{\partial \varepsilon_{ij}^o}{\partial \sigma_{kl}}\right)_T \equiv S_{ijkl} \quad (6)$$

2.4 Differential Form of Internal Energy and Free Energies

Our differential definition of internal energy with stress and strain work is:

$$dU = TdS + \sigma_{ij}d\varepsilon_{ij}^o \quad (7)$$

The internal energy relations to our enthalpy, Helmholtz free energy, and Gibbs free energy are:

$$H = U - \sigma_{ij}\varepsilon_{ij}^o \quad (8)$$

$$A = U - TS \quad (9)$$

$$G = U - TS - \sigma_{ij}\varepsilon_{ij}^o \quad (10)$$

In differential form:

$$dH = TdS - \varepsilon_{ij}^o d\sigma_{ij} \quad (11)$$

$$dA = -SdT + \sigma_{ij} d\varepsilon_{ij}^o \quad (12)$$

$$dG = -SdT - \varepsilon_{ij}^o d\sigma_{ij} \quad (13)$$

3 Introduction

Pressure waves such as sound waves and seismic waves are generally well understood phenomena but over many years and scientific fields have increasingly become useful as a means of probing the structure and behavior in a wide range system sizes from Brillouin light scattering techniques to asteroseismology. The basic physical model for any wave is the wave equation. Pressure waves are mechanical and their wave equations can be derived purely by applying Lagrange's second equation to the thermodynamic equation of state and a continuity equation. The results of which for isotropic media look something like this:

$$\frac{\partial^2 p}{\partial t^2} = \left(\frac{\partial p}{\partial \rho} \right)_S \nabla^2 p,$$

where $\left(\frac{\partial p}{\partial \rho} \right)_S = c^2$ the propagation speed. In an ideal gas, it is trivial to show that this only depends on the temperature. in an anisotropic material using Einstein notation, they look like this:

$$\partial_{tt} u_i = \frac{1}{\rho} \left(\frac{\partial \sigma_{ij}}{\partial \varepsilon_{kl}^o} \right)_S \partial_j \partial_l u_k$$

where u_i is the displacement. The adiabatic stiffness tensor in the parenthesis can be difficult to measure so we seek in this derivation to related it to the more readily available isothermal stiffness tensor.

3.1 Derivation

We start a triple product rule that relates the adiabatic stiffness tensor to two other quantities:

$$\left(\frac{\partial \sigma_{kl}}{\partial \varepsilon_{ij}^o} \right)_S \left(\frac{\partial \varepsilon_{ij}^o}{\partial S} \right)_{\sigma_{kl}} \left(\frac{\partial S}{\partial \sigma_{kl}} \right)_{\varepsilon_{ij}^o} = -1 \quad (14)$$

$\left(\frac{\partial \sigma_{kl}}{\partial \varepsilon_{ij}^o} \right)_S$ is the adiabatic stiffness tensor. The goal of this derivation is to find an expression that relates this term to the isothermal stiffness tensor. To this end, we must find expressions for the other terms in Equation 14.

We first find an expression for the second term in Equation 14, $\left(\frac{\partial \varepsilon_{ij}^o}{\partial S} \right)_{\sigma_{kl}}$. This term represents the change in strain due to a change in entropy at constant stress. We can expand this term using the chain rule:

$$\left(\frac{\partial \varepsilon_{ij}^o}{\partial S}\right)_{\sigma_{kl}} = \left(\frac{\partial \varepsilon_{ij}^o}{\partial T}\right)_{\sigma_{kl}} \left(\frac{\partial T}{\partial S}\right)_{\sigma_{kl}} \quad (15)$$

The first term on the right hand side of Equation 15 is simply the coefficient of thermal expansion at constant stress as defined in Equation 4:

$$\left(\frac{\partial \varepsilon_{ij}^o}{\partial T}\right)_{\sigma_{kl}} \equiv (\alpha_{ij})_{\sigma_{kl}}$$

We must find an expression for the second term on the right hand side of Equation 15, $\left(\frac{\partial T}{\partial S}\right)_{\sigma_{kl}}$. This is the change in temperature due to change in entropy at constant stress. In order to obtain this expression, we use the chain rule to expand the change in enthalpy due to a change in entropy at constant stress:

$$\left(\frac{\partial H}{\partial S}\right)_{\sigma_{kl}} = \left(\frac{\partial H}{\partial T}\right)_{\sigma_{kl}} \left(\frac{\partial T}{\partial S}\right)_{\sigma_{kl}} \quad (16)$$

In order to solve Equation 16 for $\left(\frac{\partial T}{\partial S}\right)_{\sigma_{kl}}$, we must find expressions for the first two terms in Equation 16. We start with an expression for enthalpy in differential form:

$$dH = TdS - \varepsilon_{kl}^o d\sigma_{kl} \quad (17)$$

Since we are under the condition of constant stress, Equation 17 can be solved assuming $d\sigma_{kl} = 0$:

$$\left(\frac{\partial H}{\partial S}\right)_{\sigma_{kl}} = T \quad (18)$$

The first term on the right hand side of Equation 16 is the heat capacity at constant stress as defined in Equation 2.

$$\left(\frac{\partial H}{\partial T}\right)_{\sigma_{kl}} \equiv c_{\sigma_{kl}}$$

Substituting Equations 2 and 18 back into Equation 16:

$$\begin{aligned} T &= c_{\sigma_{kl}} \left(\frac{\partial T}{\partial S}\right)_{\sigma_{kl}} \\ \left(\frac{\partial T}{\partial S}\right)_{\sigma_{kl}} &= \frac{T}{c_{\sigma_{kl}}} \end{aligned} \quad (19)$$

We can now substitute Equations 4 and 19 into Equation 15 to obtain the second term in Equation 14:

$$\left(\frac{\partial \varepsilon_{ij}^o}{\partial S}\right)_{\sigma_{kl}} = (\alpha_{ij})_{\sigma_{kl}} \left(\frac{T}{c_{\sigma_{kl}}}\right) \quad (20)$$

Next we must find an expression for the third term in Equation 14, $\left(\frac{\partial S}{\partial \sigma_{kl}}\right)_{\varepsilon_{ij}^o}$, which represents the change in entropy due to a change in stress at constant strain. An alternative expression for this term can be found using the Maxwell relation from internal energy:

$$\left(\frac{\partial T}{\partial \varepsilon_{ij}^o}\right)_S = \left(\frac{\partial \sigma_{ij}}{\partial S}\right)_{\varepsilon_{ij}^o} \quad (21)$$

We use again use the triple product rule, this time including the change in temperature due to a change in strain at constant entropy:

$$\left(\frac{\partial T}{\partial \varepsilon_{ij}^o}\right)_S \left(\frac{\partial S}{\partial T}\right)_{\varepsilon_{ij}^o} \left(\frac{\partial \varepsilon_{ij}^o}{\partial S}\right)_T = -1 \quad (22)$$

Next we find an expression for the second term in Equation 22, $\left(\frac{\partial S}{\partial T}\right)_{\varepsilon_{ij}^o}$, which represents the change in entropy due to a change in temperature at constant strain. We start by using the chain rule to expand, $\left(\frac{\partial U}{\partial S}\right)_{\varepsilon_{ij}^o}$, which is the change in internal energy due to a change in entropy at constant strain:

$$\left(\frac{\partial U}{\partial S}\right)_{\varepsilon_{ij}^o} = \left(\frac{\partial U}{\partial T}\right)_{\varepsilon_{ij}^o} \left(\frac{\partial T}{\partial S}\right)_{\varepsilon_{ij}^o} \quad (23)$$

We use an expression for internal energy in differential form:

$$dU = TdS - pdV \quad (24)$$

Since strain is held constant, we assume that volume is also constant ($dV = 0$):

$$\begin{aligned} dU &= TdS \\ \left(\frac{\partial U}{\partial S}\right)_{\varepsilon_{ij}^o} &= T \end{aligned} \quad (25)$$

The first term on the right hand side of Equation 23, $\left(\frac{\partial U}{\partial T}\right)_{\varepsilon_{ij}^o}$, was defined in Equation 1 as the heat capacity at constant strain:

$$\left(\frac{\partial U}{\partial T}\right)_{\varepsilon_{ij}^o} \equiv c_{\varepsilon_{ij}^o}$$

Substituting Equations 1 and 25 into Equation 23 gives us an expression for the second term in Equation 22:

$$\begin{aligned}
T &= c_{\varepsilon_{ij}^o} \left(\frac{\partial T}{\partial S} \right)_{\varepsilon_{ij}^o} \\
\left(\frac{\partial T}{\partial S} \right)_{\varepsilon_{ij}^o} &= \frac{T}{c_{\varepsilon_{ij}^o}} \\
\left(\frac{\partial S}{\partial T} \right)_{\varepsilon_{ij}^o} &= \frac{c_{\varepsilon_{ij}^o}}{T}
\end{aligned} \tag{26}$$

Next we find an expression for the third term in Equation 22. We start with the Maxwell relation for Helmholtz free energy:

$$\left(\frac{\partial S}{\partial \varepsilon_{ij}^o} \right)_T = - \left(\frac{\partial \sigma_{ij}}{\partial T} \right)_{\varepsilon_{ij}^o} \tag{27}$$

Strain can be written in differential form as:

$$d\varepsilon_{ij}^o = S_{ijkl} d\sigma_{kl} + \alpha_{ij} dT \tag{28}$$

Since the strain is constant ($d\varepsilon_{ij}^o = 0$):

$$\begin{aligned}
0 &= S_{ijkl} d\sigma_{kl} + \alpha_{ij} dT \\
-S_{ijkl} d\sigma_{kl} &= \alpha_{ij} dT \\
-S_{ijkl} \left(\frac{\partial \sigma_{kl}}{\partial T} \right)_{\varepsilon_{ij}^o} &= \alpha_{ij}
\end{aligned} \tag{29}$$

We multiply both sides of Equation 29 by the stiffness tensor, C_{klij} :

$$\begin{aligned}
(C_{klij})(-S_{ijkl}) \left(\frac{\partial \sigma_{kl}}{\partial T} \right)_{\varepsilon_{ij}^o} &= C_{klij} \alpha_{ij} \\
- \left(\frac{\partial \sigma_{kl}}{\partial T} \right)_{\varepsilon_{ij}^o} &= C_{klij} \alpha_{ij}
\end{aligned} \tag{30}$$

Substituting Equation 27 into Equation 30 and swapping indices:

$$\begin{aligned}
\left(\frac{\partial S}{\partial \varepsilon_{ij}^o} \right)_T &= C_{ijkl} \alpha_{kl} \\
\left(\frac{\partial \varepsilon_{ij}^o}{\partial S} \right)_T &= (C_{ijkl} \alpha_{ij})^{-1}
\end{aligned} \tag{31}$$

We now substitute Equations 26 and 31 into Equation 22:

$$\left(\frac{\partial T}{\partial \varepsilon_{ij}^o}\right)_S \left(\frac{c_{\varepsilon_{ij}^o}}{T}\right) (C_{ijkl}\alpha_{ij})^{-1} = -1$$

$$\left(\frac{\partial T}{\partial \varepsilon_{ij}^o}\right)_S = -\left(\frac{T}{c_{\varepsilon_{ij}^o}}\right) (C_{ijkl}\alpha_{ij})$$

Again using the Maxwell relation from Equation 21:

$$\left(\frac{\partial \sigma_{ij}}{\partial S}\right)_{\varepsilon_{ij}^o} = \left(\frac{\partial T}{\partial \varepsilon_{ij}^o}\right)_S = -\left(\frac{T}{c_{\varepsilon_{ij}^o}}\right) (C_{ijkl}\alpha_{ij})$$

$$\left(\frac{\partial S}{\partial \sigma_{ij}}\right)_{\varepsilon_{ij}^o} = -\left(\frac{c_{\varepsilon_{ij}^o}}{T}\right) (C_{ijkl}\alpha_{ij})^{-1} \quad (32)$$

We can now substitute Equations 20 and 32 back into Equation 14:

$$\left(\frac{\partial \sigma_{kl}}{\partial \varepsilon_{ij}^o}\right)_S (\alpha_{ij})_{\sigma_{kl}} \left(\frac{T}{c_{\sigma_{kl}}}\right) \left[-\left(\frac{c_{\varepsilon_{ij}^o}}{T}\right) (C_{ijkl}\alpha_{ij})^{-1}\right] = -1$$

$$\left(\frac{\partial \sigma_{kl}}{\partial \varepsilon_{ij}^o}\right)_S = \left(\frac{c_{\sigma_{kl}}}{c_{\varepsilon_{ij}^o}}\right) C_{ijkl} \quad (33)$$

4 References

5 Appendices

5.1 Maxwells Relations

The Maxwell relation for the internal energy U (Equation 7) is:

$$\left(\frac{\partial T}{\partial \varepsilon_{ij}^o}\right)_{S, \varepsilon_{kl}^o \neq ij} = \left(\frac{\partial \sigma_{ij}}{\partial S}\right)_{\varepsilon_{kl}^o} \quad (34)$$

On the left, all strains are held constant except ε_{ij}^o .

Likewise, the Maxwell relation for enthalpy H (Equation 11) is:

$$\left(\frac{\partial T}{\partial \sigma_{ij}}\right)_{S, \sigma_{kl} \neq ij} = -\left(\frac{\partial \varepsilon_{ij}^o}{\partial S}\right)_{\sigma_{kl}} \quad (35)$$

The Maxwell relation for Helmholtz free energy A (Equation 12) is:

$$-\left(\frac{\partial S}{\partial \varepsilon_{ij}^o}\right)_{T, \varepsilon_{kl}^o \neq ij} = \left(\frac{\partial \sigma_{ij}}{\partial T}\right)_{\varepsilon_{kl}^o} \quad (36)$$

The Maxwell relation for Gibbs free energy A (Equation 13) is:

$$\left(\frac{\partial S}{\partial \sigma_{ij}}\right)_{T, \sigma_{kl} \neq ij} = \left(\frac{\partial \varepsilon_{ij}^o}{\partial T}\right)_{\sigma_{kl}} \quad (37)$$